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Observations on nickel-free-beryllium-free fixed prosthodontic alloys.

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Abstract

Mechanical properties, microstructural features, heat treatment characteristics, composition and electrochemical behavior of two nickel-free-beryllium-free fixed prosthetic alloys were studied. Properties of two alloys were similar. The high modulus of elasticity, yield strength and hardness combined with low ductility make finishing and polishing of these alloys difficult.

Continued fluctuations in the price of gold and other precious metals has prompted intense interest in the development of alloys comprised of less expensive constituents. Heretofore, nickel (60-68%) and chromium (12-20%) have been components of most available products and beryllium (0.5-2%) an additional constituent of others.

Reactions to nickel-containing alloys used in the fabrication of jewelry, medical implants and surgical devices as well as the potential hazards of beryllium ingestion or inhalation have been reported.¹⁻⁶ Presently, advertising literature for nickel and beryllium-containing alloys classified as acceptable by the American Dental Association must contain cautionary statements as to the impropriety of grinding or polishing the alloy without adequate ventilation or the fabrication of dental prostheses for patients with a known nickel sensitivity.⁷

Recently, base metal alloys devoid of nickel and beryllium have become commercially available for use in fixed prosthodontic procedures. The present report is based upon data and observations on two nickel-free and beryllium-free fixed prosthodontic alloys, Biocast⁺ and Neobond II,[#]

Materials and methods

Castings for the determination of mechanical properties and micro-structural features were fabricated by conventional lost-wax dental laboratory procedures. Wax patterns for the test specimens were invested in

⁺ Biocast; Rx Jeneric Gold Company, Wallingford, CT 06492.

[#] Neobond II, Neoloy Products Inc., Posen, IL 60469.

phosphate-bonded refractories.⁵ Wax elimination and casting were conducted in accordance with the respective alloy manufacturer's instructions. Melting and casting were accomplished with the aid of an automatic induction casting machine.⁶ Casting temperatures were 2,660 F and 2,665 F for Biocast and Neobond II, respectively. The cast molds were bench cooled to room temperature prior to divestment of the test pieces.

Dimensions of the specimens for the measurement of tensile properties were within the tolerances prescribed by American Dental Association No. 14 for dental chromium-cobalt casting alloy.⁸ Six tensile specimens were subjected to heat treatment by a simulated porcelain firing cycle. The cycle included four consecutive heat treatments: Alloy conditioning specimens were heated from 1,200 F to 1,950 F and kept at the latter temperature five minutes before removing from the furnace; opaque application specimens were heated from 1,200 F to 1,825 F, removed from the furnace on reaching 1,825 F, and cooled to room temperature; body porcelain application specimens were heated from 1,200 F to 1,775 F and removed immediately from the furnace; and glaze application specimens were heated from 1,200 F to 1,800 F and cooled to room temperature on reaching 1,800 F. Cooling after each step of the treatment cycle was done in open air. An equal number of specimens were retained in the as-cast condition. Two additional tensile bars were sectioned in half and used to assess the electrochemical behavior of the test alloys in a corrosive medium.

⁵ For Biocast alloy: Ceramigold 2, Whip-Mix Corp., Louisville, KY 40217.

For Neobond II: Neoloy Hi-Heat Investment, Neoloy Products Inc.,
Posen, IL 60469.

⁶ Electromatic III, Howmedica Inc., Chicago, IL 60632.

Hardness and metallographic specimens were 13 mm X 3 mm cast discs. The test pieces were mounted in plastic and polished sequentially with 240-600-grit abrasive papers, diamond paste (6 μm) and alumina (0.3 μm and 0.05 μm). Metallographic specimens were etched by immersion in a solution of 92% HCl, 5% H_2SO_4 and 3% HNO_3 by volume.

Subsequent to the determination of as cast microstructure and hardness, the discs were removed from their plastic mounts and subjected to time and temperature controlled heat treatments. All metallographic and some hardness specimens were subjected to the simulated porcelain firing cycle employed in the treatment of tensile bars. The remaining hardness specimens were subjected to serial heat treatments for the determination of the softening temperature range of the test alloys.

Softening temperatures were obtained by monitoring changes in the hardness of discs exposed to eight successive five-minute heat treatments at 200° intervals from 400 to 1,800 F. All of these treatments were terminated by water quenching. Hardness was measured after treatment of the discs at each temperature.

Tensile properties of as cast and heat-treated bars were determined on a constant displacement rate testing machine⁺⁺ at a crosshead speed of 0.02 inch per minute. Elongation was measured over a one-inch gauge length with a breakaway extensometer.^{##} Hardness (DPN) values were obtained with the use of a testing machine^{§§} equipped with a 136-degree square-based

⁺⁺ Instron Universal Testing Machine, Instron Engineering Corp., Canton, MA 02021.

^{##} Strain Gauge Extensometer, Model LG-51-12, Instron, Corp., Canton, MA 02021.

^{§§} Kentral Hardness Tester, Model MC-1, Riehle Testing Machines, East Moline, IL. 61244.

diamond pyramid indenter.

Acid etched surfaces of the metallographic specimens were observed with the aid of an optical microscope²² at a magnification of 400X. Constituents of the "as received" alloys were determined semiquantitatively by atomic absorption spectrophotometry.¹¹

Laboratory evaluation of the potential corrosion resistance of the test alloys was accomplished by analysis of the electrochemical behavior of each alloy in a corrosive medium. Electrochemical profiles of each alloy were determined by cyclic potentiodynamic polarization techniques with the aid of a programmable potentiostat.¹¹ Changes in current density in milliamperes per square centimeter (ma/cm²) of specimen area were monitored continuously over a potential range of negative one volt to positive one volt versus a saturated calomel electrode (SCE) at a scan rate of 20 millivolts per second. The test medium consisted of one part by volume of lactated Ringer's solution¹¹¹ and 4.5 parts by volume deionized water producing a solution with a chloride concentration comparable to that of human saliva.⁹

²² Vickers 55 Metallograph, Cook, Troughton and Simms, Inc., Molden, MA 02148.

¹¹ Spectrophotometer, Model 403, Perkin-Elmer Corp., Norwalk, CT 06850.

¹¹ Potentiostat/Galvanostat, Model 173 and Universal Programmer, Model 175, Analytical Instrument Division, Princeton Applied Research Corp., Princeton, NJ 08540.

¹¹¹ Cutter Laboratories, Inc., Berkeley, CA 94710.

Results

The data on the mechanical properties of electrochemical behavior of the test alloys are shown in the Table. As cast mechanical properties of the two alloys differed only with respect to percent elongation and hardness. Exposure of Neobond II to the simulated porcelain firing cycle elicited a 19 percent increase in hardness and a 67 percent decrease in elongation.

Analysis of the electrochemical profiles of the test alloys revealed that both Biocast and Neobond II were weakly passive in the as cast condition when at equilibrium with the test medium. Respective equilibrium (corrosion) potentials for Biocast and Neobond II were -0.385 volts versus SCE and -0.450 volts versus SCE. Exposure to the simulated porcelain firing cycle did not markedly alter the values of the corrosion potential or corrosion current density of Biocast. However, the alloy exhibited strong passivity at equilibrium subsequent to heat treatment procedures. Neobond II remained weakly passive at equilibrium following exposure to the simulated porcelain firing cycle although the corrosion potential became markedly more positive (noble).

The response of the test alloys to serial heat treatments over the 400 F to 1,800 F temperature range is shown in Figure 1. Both alloys exhibited a gradual increase in hardness over a 400 F to 1,200 F range. Increases in hardness at temperatures above 1,200 F were not observed in specimens of either material.

Microstructural features of the alloys are shown in Figure 2. The as-cast microstructure of Biocast was cored whereas that of Neobond II exhibited a continuous grain boundary network and intragranular phase. Exposure of the test alloys to the simulated porcelain firing cycle did

not markedly alter the microstructural characteristic of Biocast. However, microscopic examination of heat treated specimens of Neobond II revealed the presence of granular and asicular precipitates.

Findings from the quantitative analysis of the alloys revealed that Neobond II is based upon a cobalt (~65.2%)-chromium (~24.5%) system with minor additions of iron (~3.8%), molybdenum (~1.2%), copper (~0.97%), silicon (~0.41%) and tin (~4%). The cobalt (~69%)-chromium (~26%) binary of Biocast was modified with molybdenum (~1.9%), manganese (~0.80%), iron (~.50%).

Discussion

From the available data, it would appear that the values for the mechanical properties of Neobond II and Biocast are comparable to those of base metal partial denture alloys.¹⁰⁻¹² Modulus of elasticity values of both alloys approach 30 million pounds per square inch. These values are about twice those of the high-fusing gold alloys.¹³ Conversely, the elongation of these cobalt-chromium alloys is six to twenty times less than that of the high-fusing noble alloys.

The high modulus of elasticity (rigidity) and relatively high yield strength suggests the usefulness of these alloys for the casting of thin copings and retainers as well as for the fabrication of long span fixed partial dentures. However, when coupled with high hardness and low ductility, these properties impede minor adjustment, polishing and finishing and adaptation of margins.

Alterations in some of the properties of Neobond II subsequent to exposure of test specimens to the simulated porcelain firing cycle, appear to be related to microstructural changes. Increased hardness and reduced ductility

are attributed to precipitate formation.

Data from the electrochemical profile analyses suggest that as cast specimens of the test alloys may not passivate spontaneously in the oral environment. The relatively negative (active) corrosion potential and high current density exhibited by as cast specimens of Neobond II suggests that this alloy may be less corrosion resistant than Biocast. Subsequent to heat treatment by the porcelain firing cycle, the formation of protective films on Biocast specimens (passivation) and the increase of the corrosion potential and concomittant reduction corrosion current density exhibited by Neobond II specimens suggests an increase in corrosion resistance. It is doubtful that the observed differences in the electrochemical behavior of the two alloys would be discernible clinically.

The greatest problems associated with the clinical use of base-metal fixed prosthodontic alloys are difficulties in casting these materials using equipment, materials and techniques designed for the centrifugal casting of gold alloys. Thin sections of castings fabricated from base metal alloys are often incomplete and fine detail is prone to obliteration by rounding. Full coverage castings fabricated for preparations with relatively parallel walls often fail to seat completely. Recent work has suggested that modifications to investing techniques such as alteration of liquid-powder ratios and method of compensatory expansion are required to produce acceptable castings from cobalt-chromium based fixed prosthodontic alloys.¹⁴ Further work designed to assess porcelain application techniques, soldering methods and tissue reactions of these alloys are in progress.

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Legends for figures

Figure 1. Effect of heat-treatment temperature on the hardness of two fixed prosthodontic alloys.

Figure 2. Microstructures of nickel free-beryllium free fixed prosthodontic alloys (original magnification, 400X). A, Biocast, as cast; B, Biocast, heat treated by the simulated porcelain firing cycle; C, Neobond II, as cast; D, Neobond, heat treated by the simulated porcelain firing cycle.

TABLE. Properties of two high-fusing fixed prosthodontic alloys.

Property	Biocast		Neohond II	
	As cast	Heat-treated*	As cast	Heat-treated*
Tensile Strength ($\times 10^3$ psi)	$103 \pm 10^+$	$111 \pm 12^+$	$102 \pm 6^+$	$99 \pm 6^+$
Yield Strength ⁺⁺ ($\times 10^3$ psi)	79 ± 5	78 ± 5	87 ± 8	91 ± 3
Modulus of Elasticity ($\times 10^6$ psi)	28 ± 2	30 ± 1	31 ± 2	31 ± 2
Elongation (%)	1 ± 0.3	1 ± 0.2	3 ± 1.0	1 ± 1.0
Hardness (DPN)	390 ± 4	426 ± 1.5	290 ± 7	344 ± 7
Corrosion Potential (mV vs. SCE) [#]	-385	-330	-450	0
Corrosion Current Density ($\times 10^{-3}$ ma/cm ²) ^{**}	5.6	3.25	35.5	0.91
Equilibrium Condition	weakly passive	passive	weakly passive	weakly passive

* Simulated porcelain firing cycle.

+ Standard deviation.

++ 0.2% offset.

Millivolts versus a saturated calomel electrode.

** Milliamperes per square centimeter.



